Nonadiabatic couplings from time-dependent density functional theory: Formulation in the Casida formalism and practical scheme within modified linear response

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We present an efficient method to compute nonadiabatic couplings (NACs) between the electronically ground and excited states of molecules, within the framework of time-dependent density functional theory (TDDFT) in frequency domain. Based on the comparison of dynamic polarizability formulated both in the many-body wave function form and the Casida formalism, a rigorous expression is established for NACs, which is similar to the calculation of oscillator strength in the Casida formalism. The adiabatic local density approximation (ALDA) gives results in reasonable accuracy as long as the conical intersection (ci) is not approached too closely, while its performance quickly degrades near the ci point. This behavior is consistent with the real-time TDDFT calculation. Through the use of modified linear response theory together with the ground-state-component separation scheme, the performance of ALDA can be greatly improved, not only in the vicinity of ci but also for Rydberg transitions and charge-transfer excitations. Several calculation examples, including the quantization of NACs from the Jahn-Teller effect in the H₃ system, have been given to show that TDDFT can efficiently give NACs with an accuracy comparable to that of wave-function-based methods. © 2007 American Institute of Physics. [DOI: 10.1063/1.2755665]

I. INTRODUCTION

As the basis for modern quantum study of molecular systems, the Born-Oppenheimer theory provides us with a universal way to distinguish the slowly moving nuclei from electrons. In this treatment, the nonadiabatic coupling (NAC) terms, together with the adiabatic potential energy surfaces, determine the driving forces that govern the motion of atoms in the molecular system. Due to the large mass difference between electrons and nuclei, the NAC terms are usually assumed to be quite small and the Born-Oppenheimer approximation can be applied, which ignores the NAC terms and thus completely separates the electronic and nuclear motions. This approximation is extremely reliable for describing near-equilibrium properties of most molecules and many ab initio theories are built upon it, by which there is no need for the full quantum-mechanical treatment of molecular systems. However, this approximation will break down if there exists degenerate states: NACs become infinite at the degeneracy points, e.g., conical intersections (ci’s). The existence of ci has important consequences for the molecular dynamics, not only permitting the efficient nonadiabatic transitions between potential energy surfaces but also being the source for numerous phenomena that are considered as topological effects, including the well-known geometric phase (Berry phase) effect. Experimental observations of the geometric phase effects have been realized in recent years, attracting wide attention to the study of ci on this aspect. It is now recognized that ci can appear frequently in the absence of any symmetry considerations, making the geometric phase effect and the occurrence of nonadiabatic transitions more commonplace phenomena.

For the theoretical description of molecular dynamics near ci, it is necessary to compute NACs together with adiabatic potential energy surfaces. Research on this aspect has been long carried out using wave-function-based methods and much work has been done. However, as the molecular system becomes larger, the computational cost of these quantum chemistry approaches rapidly increases and actually becomes unaffordable. How to obtain NACs both accurately and efficiently is a long-standing important task. A natural consideration for the more efficient approach would be the density-based methods, of which time-dependent density functional theory (TDDFT) seems to be the most eligible one, which has gained enormous popularity in studying excited states of molecular systems. Inheriting the picture of noninteracting particles from density functional theory (DFT), it provides a formally exact and computationally efficient treatment for calculating electronic excitations. The main problem is that, although the adiabatic potential surfaces can be routinely calculated by TDDFT in an efficient way, it is not so for the computation of NACs at present. In contrast to the extensive studies of NACs by ab initio wave-function-based methods, the investigation of NACs by TDDFT is seldom found in literature. Chernyak and Mukamel have given a closed expression of NACs in TDDFT, but application of their scheme to specific molecules has not been carried out yet. Baer has developed a real-time TDDFT approach to calculate NACs for molecules, and applied the method to the H₃ system, using the adiabatic...
local density approximation (ALDA). The result is rather good but deteriorates near ci. The real-time TD-DFT approach is in principle equivalent to the frequency-domain TD-DFT approaches in the linear response (LR) regime, while the latter is more favored by chemists. One of the most popular frequency-domain methods is the Casida formalism, known as time-dependent density functional response theory (TD-DFT) and implemented in many standard quantum chemistry codes. However, it is surprising to find that the calculation of NACs by the Casida formalism method often used in treating NACs in the direct way, e.g., the finite-difference DFT, but in turn it may pose a practical problem for computing NACs in the vicinity of ci or for Rydberg and charge-transfer excitations. This accounts for the efficiency of TD-DFT to NACs may come from the intrinsic feature of ALDA near ci is yet to be explored.

The reason for the rare investigation of the applicability of TD-DFT to NACs may come from the intrinsic feature of TD-DFT: Not the many-body wave function but the electronic density and Kohn-Sham (KS) orbitals are explicitly treated in TD-DFT. This accounts for the efficiency of TD-DFT, but in turn it may pose a practical problem for computing NACs in the direct way, e.g., the finite-difference DFT, but in turn it may pose a practical problem for computing NACs in the direct way. The lack of many-body wave functions seems conceptually difficult for the derivation of NACs; however, a further look into the Casida formalism reveals that the many-body wave function representation of the dynamic polarizability can be exactly transformed into an expression merely constructed by KS eigenenergies, orbitals, and kernels. This leads to the successful calculation of oscillator strengths by TDDFT as the excitation energy 0 can be routinely calculated by TDDFT as the excitation energy.

For NACs between the ground state and the Ith excited state, we get

\[ A_{ij,\mu} = \frac{\langle \Psi_i | \partial_{\mu} \hat{H} | \Psi_j \rangle}{E_j - E_i}, \quad i \neq j, \]

where \( E_i \) is the eigenenergy of the Ith eigenstate, i.e., \( \hat{H} \Psi_i = E_i \Psi_i \). This transformation is due to the simple relation that

\[ 0 = \langle \Psi_i | \partial_{\mu} \hat{H} | \Psi_j \rangle = \langle \Psi_i | \partial_{\mu} \hat{H} | \Psi_j \rangle - \partial_{\mu} E_j \delta_{ij} + \langle \Psi_i | \partial_{\mu} | \Psi_j \rangle (E_j - E_i). \]

In the following we will write \( \partial_{\mu} \hat{H} \) as \( \hat{h}_{\mu} \). For NACs between the ground state and the Ith excited state, we get

\[ A_{0I,\mu} = \frac{\langle \Psi_0 | \hat{h}_{\mu} | \Psi_I \rangle}{E_I - E_0} = \frac{\langle \Psi_0 | \hat{h}_{\mu} | \Psi_I \rangle}{\omega_I}, \]

since the difference of \( E_I \) and \( E_0 \) can be routinely calculated by TDDFT as the excitation energy \( \omega_I \).

To compute NACs from TD-DFT, we introduce a perturbation,

\[ \delta_{\text{app}0}(\mathbf{R}, t) = \hat{h}_{\mu}(\mathbf{R}) \xi_{\mu}(\mathbf{R}, t), \]

as done by Chernyak and Mukamel. Note that we use atomic units all through our derivation and therefore \( \hbar = 1 \). We next consider the time-domain linear response function \( \alpha_{\mu\nu}(\mathbf{R}, t) \) with respect to the driving field \( \xi_{\mu}(\mathbf{R}, t) \),

\[ \delta(\hat{h}_{\mu}(\mathbf{R}, t)) = \int_{-\infty}^{t} dt' \alpha_{\mu\nu}(\mathbf{R}, t - t') \xi_{\nu}(\mathbf{R}, t'), \]

and the corresponding frequency-domain dynamic polarizability,

\[ \alpha_{\mu\nu}(\mathbf{R}, \omega) = \int_{0}^{\infty} dt \exp(i\omega t) \alpha_{\mu\nu}(\mathbf{R}, t) dt \]

For convenience we will omit \( \mathbf{R} \) in the following expressions. The convolution theorem gives

\[ \alpha_{\mu\nu}(\omega) = \frac{\delta(\hat{h}_{\mu}(\omega))}{\xi_{\nu}(\omega)}. \]

Since

\[ A_{ij,\mu} = \langle \Psi_i | \partial_{\mu} | \Psi_j \rangle, \]

A rigorous formulation

The first-order NACs are defined as the matrix element of the nuclear coordinate derivative \( \partial R_\mu \), with \( \mu \) representing the x, y, z component and the atom index. It is written as

\[ A_{ij,\mu} = \langle \Psi_i | \partial_{\mu} | \Psi_j \rangle = \langle \Psi_i | \frac{\partial}{\partial R_\mu} | \Psi_j \rangle, \]

(1)

where \( \Psi_i \) is the many-body wave function of the Ith eigenstate. Note that \( A \) is real and anti-Hermitian for isolated systems, i.e., \( A_{ij,\mu} = -A_{ji,\mu} \). Equation (1) can be rewritten as

\[ A_{ij,\mu} = \frac{\langle \Psi_i | \partial_{\mu} \hat{H} | \Psi_j \rangle}{E_j - E_i}, \quad i \neq j, \]

(2)

II. METHOD

A. Computation of NACs from the Casida formalism (TD-DFT):

The present paper is organized as follows. In Sec. II, we give the theoretical aspects of our method. First, a rigorous formulation for NACs is achieved in the Casida formalism; then, we extend this method within MLR to improve the performance of ALDA, for which the ground-state-component separation scheme is presented. In Sec. III, the practical implementation and computational details in the plane-wave pseudopotential framework are given. In Sec. IV, we apply our method to various molecular systems to investigate NACs either in the vicinity of ci or for Rydberg and charge-transfer excitations. In Sec. V, we conclude our work.
where $P_{ijr}$ is the density-matrix element, $h_{ijr,\mu}$ is the matrix element of the $\hat{h}_\mu$ operator, and $\chi$ is the generalized susceptibility, it follows that

$$
\alpha_{\mu\mu}(\omega) = -\sum_{ijr,\mu} h_{ijr,\mu} \chi_{ijr,\mu}(\omega) h_{ijr\mu}(\omega),
$$

where $\chi_{ijr,\mu}(\omega)$ is the generalized susceptibility.

Making use of the sum-over-states (SOS) representation of the susceptibility as derived by the general time-dependent response theory using the creation and annihilation operators $(\hat{a}_{\mu}^\dagger)$ and $(\hat{a}_{\mu})$, we can also write the expression of the dynamic polarizability into the following form:

$$
\alpha_{\mu\mu}(\omega) = -\sum_{i} 2(E_i - E_0) \langle \Psi | \hat{h}_\mu | \Psi \rangle \langle \Psi | \hat{h}_\mu | \Psi \rangle (E_i - E_0)^{-2} \omega^{-2}.
$$

From Eq. (8), we can also write the expression of the dynamic polarizability into the following form:

$$
\alpha_{\mu\mu}(\omega) = -2 \sum_{ijr} \chi_{ijr,\mu}(\omega) h_{ijr,\mu}(\omega) \chi_{ijr,\mu}(\omega),
$$

where $(\Re \delta P_{ijr})(\omega)$ denotes the Fourier transform of the real part of $\delta P_{ijr}(t)$. Following the pioneering work of Casida, the relationship of $(\Re \delta P)(\omega)$ and $\chi(\omega)$, or equivalently, $\chi_{\text{app}}(\omega)$, can be derived in the same way as

$$
(\Re \delta P)(\omega) = S^{1/2}[\omega^2 \mathbf{1} - \mathbf{\Omega}(\omega)]^{-1} S^{1/2} \chi_{\text{app}}(\omega),
$$

where

$$
S_{ijr,\mu} = \frac{\partial_{\mu} \delta_{\mu} \delta_{ij} \delta_{\mu j}}{(E_i - E_j)(\epsilon_{i\mu} - \epsilon_{j\mu})},
$$

which is constructed by the occupation number $f_j$ and KS eigenenergies $\epsilon_j$, and

$$
\Omega_{ijr,\mu} = \delta_{\mu r} \delta_{\mu j} (\epsilon_{i\mu} - \epsilon_{j\mu})^2 + 2(f_{ijr} - f_{ijr})(\epsilon_{i\mu} - \epsilon_{j\mu})
\times K_{ijr,\mu} (f_{ijr} - f_{ijr})(\epsilon_{i\mu} - \epsilon_{j\mu}).
$$

The coupling matrix $\mathbf{K}$ is calculated as

$$
K_{ijr,\mu} = \int \int \psi^*_{ijr}(\mathbf{r}) \psi_{ijr}(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_{ijr}(\mathbf{r}') \psi_{ijr}(\mathbf{r}') d\mathbf{r} d\mathbf{r}'.
$$

$$
\alpha_{\mu\mu}(\omega) = 2h_{\mu}^{1/2}S^{-1/2}[\Omega(\omega) - \omega^2 \mathbf{1}]^{-1} S^{-1/2} h_{\mu}. \tag{15}
$$

The excitation energies can be obtained from the pole condition, i.e., the pseudoeigenvalue equation

$$
\Omega F_j = \omega_j F_j, \tag{20}
$$

where the eigenvalue $\omega_j$ is the squared excitation energy of the $j$th transition, and $F_j$ is the corresponding eigenvector. When $F_j$ is normalized, we can use the spectral expansion to get

$$
\{\Omega - \omega^2 \mathbf{1}\}^{-1} = \sum_j \frac{F_j F_j^\dagger}{\omega_j^2 - \omega^2}. \tag{21}
$$

Substituting Eq. (19) by Eq. (21), we can get

$$
\alpha_{\mu\mu}(\omega) = \sum_j \frac{2h_{\mu}^{1/2}S^{-1/2}F_j F_j^\dagger S^{-1/2} h_{\mu}}{\omega_j^2 - \omega^2}. \tag{22}
$$

Comparing with the SOS formula of Eq. (13) shows that

$$
h_{\mu}^{1/2} S^{-1/2} F_j = \omega_j^{1/2} \langle \Psi | \hat{h}_\mu | \Psi \rangle, \tag{23}
$$

so that NACs are just given by

$$
A_{\alpha\mu} = \frac{h_{\mu} S^{-1/2} F_j}{\omega_j^{3/2}}. \tag{24}
$$

It is worth noting that the above procedure is very similar to the derivation of oscillator strength in the Casida formalism. The signs of computed NACs are arbitrary in this methodology, but the relative signs can be uniquely determined by applying the continuity condition.

### B. Computation of NACs within MLR: Ground-state-component separation scheme

The computation of NACs by TDDFT requires two parts to be first calculated: One is the excitation energy, $\alpha_\omega$, and the other is $h_{\mu} S^{-1/2} F_j$ called as nonadiabatic strength term hereafter. For accurate evaluation of these two parts, using more sophisticated exchange-correlation functionals other than ALDA may be a natural option. On the other hand, it is also important to improve the methodology based on existing functionals. In our previous work, we have implemented MLR to improve TDDFT performance on the prediction of excitation energies, just using ALDA. The basic idea is to take average of excitation energies over the occupation number, and we have found that the midpoint value calculated from the response of the mid-excited state is accurate enough for general applications. Associating with the calculation of NACs, it would also be interesting to apply this averaging.
scheme. Due to the fractional form of NACs, taking a simple average would favor too much the states with small excitation energies, while the criterion of appropriate weight for taking a weighted average is not known yet. Therefore, we will test only the midpoint value. Since the essence of MLR is to take average over intermediate excited states, the performance at the midexcited state should be of significant importance. Also in practice, it is known that achieving self-consistent-field (SCF) convergence is often much easier at the midexcited state than at other intermediate ones near the degeneracy point, as discussed later.

To compute excitation energies, we use the adapted Casida equation by transforming the \( \Omega \) matrix in Eq. (20) into the nonsymmetric form

\[
\Omega_{ij,kl}^m = \delta_{ir,k} \delta_{jl} (e_{ijr}^m - e_{ij}^m)^2 + 2(f_{ij}^m - f_{ijr}^m)(e_{ijr}^m - e_{ij}^m)K_{ij,kl},
\]

where the superscript \( m \) denotes the midexcited state, in which a “half” electron is promoted from the donor orbital to the acceptor orbital. The excitation energy, \( \omega_i^m \), is then calculated by solving

\[
\Omega_i^m \psi_i^m = (\omega_i^m)^2 \psi_i^m.
\]

Contrary to the calculation of excitation energies, Eqs. (25) and (26) are not convenient for the nonadiabatic strength term. To see the reason, consider a one-electron two-level system. Equations (25) and (26) yield the KS eigenenergy difference for the excitation energy but zero for the nonadiabatic strength term because, from Eq. (24),

\[
A_\mu = -\frac{\hbar^2}{2m} \sqrt{(f_{ij}^m - f_{ijr}^m)(e_{ijr}^m - e_{ij}^m)} = 0,\]

since \( f_{ij}^m = f_{ijr}^m = 0.5 \) in the midexcited state. Apparently, this is not the practical case. A careful consideration reveals the origin of this problem: The midexcited state is a mixed state, comprising both ground and excited state components, whose contributions to NACs cancel out each other. If we just calculate NACs in the straightforward way, we can only get a canceled result. Therefore, we need to separate the pure ground-state component contributing to NACs. Procedure for the separation can be obtained along the line of Ref. 24, where the role of the partial occupation number in TD-DFRT was discussed. The system with partial occupation can be regarded as the ensemble (mixed state) of systems with integer occupation. In this regard, Casida described the response of the ensemble as the occupation-number weighted sum (average) of the individual response, yielding

\[
\chi_{ij,kl}^m(\omega) = \delta_{ir,k} \delta_{jl} \frac{f_{ijr} - f_{ij}^m}{\omega - (e_{ij} - e_{ijr})},
\]

which shows that the excitation and deexcitation processes occur simultaneously in the partially occupied system. This conclusion is based on the system of independent particles, but it can be applied seamlessly to the KS noninteracting system, because the KS self-consistent field is determined by the averaged density matrix and applies equally to the components of the ensemble. The average feature of the KS response indicates that, by using the interaction kernel and KS eigenvalues of the ensemble, as well as using the integer occupation number of each component, the individual response can be obtained. For the specific ground-state component, this procedure extracts a pure-state configuration, which uses the occupation number of the ground state while keeping other quantities of the midexcited state. The nonadiabatic strength term is then computed from the corresponding Casida equation for the pure-state configuration

\[
\Omega_{ij,kl}^m = (\omega_i^m)^2 \psi_i^m,
\]

where

\[
\Omega_{ij,kl}^m = \delta_{ir,k} \delta_{jl} (e_{ijr}^m - e_{ij}^m)^2 + 2(f_{ij}^m - f_{ijr}^m)(e_{ijr}^m - e_{ij}^m)K_{ij,kl},
\]

and \( f_{ij}^m \) is the occupation number of the \( i \)th orbital in the ground state. All other quantities with the \( m \) superscript are those in the midexcited state. The desired NACs are then computed by

\[
A_{kl,\mu} = -\frac{\hbar^2}{2m} \frac{S_{ijkl}^{-1/2} \psi_i^m}{\psi_i^m},
\]

where \( \omega_i^m \) is calculated from Eq. (26),

\[
h_{ij,kl} = h_{ij,kl}^m,
\]

and

\[
S_{ijkl}^{-1/2} = \frac{\delta_{ir,k} \delta_{jl}}{(f_{ijr}^m - f_{ij}^m)(e_{ij}^m - e_{ijr}^m)},
\]

constructed by the occupation numbers of the ground state and the eigenenergies of the midexcited state. In the formula of Eq. (31), the excitation energy is computed from the response of the midexcited state, while the nonadiabatic strength term (the numerator) is from that of the pure-state configuration. As shown in the following part of this paper, this formula indeed gives reasonably accurate NACs for several benchmark molecular applications. This indicates that correcting the ground-state KS eigenenergies is the important key to improve the calculation.

III. IMPLEMENTATION AND COMPUTATIONAL DETAILS

The implementation of our method is based on the ABINIT code,29 which is a plane-wave pseudopotential approach. All calculations are performed within adiabatic LDA/LSDA using the Perdew-Wang 92 functional,30 which is a reparametrization of the Ceperley-Alder data.31 The Troullier-Martins pseudopotentials32 generated by Khein and Allain, as well as Fritz-Haber-Institut pseudopotentials,33 are used for various atomic species. Only the \( \Gamma \) point \((k=0)\) is taken into consideration in the \( \mathbf{k} \) point sampling, which corresponds to the use of real wave functions. Convergence parameters, such as the supercell size, number of unoccupied orbitals, and kinetic energy cutoff, are examined to ensure reasonably accurate results. On the basis of the previous implementation of MLR in ABINIT,34 the supplementary work of the ground-state-component separation scheme requires almost no additional labor, since it is only necessary to construct the pure-
state configuration from the midexcited state and to apply the same calculation procedures as ordinary LR.

A. Calculation of the h matrix in the plane-wave pseudopotential approach

The matrix element, \( h_{ijr,\mu} \), can be calculated in the plane-wave pseudopotential framework as

\[
h_{ijr,\mu} = \langle \psi_i | \partial_{\mu} \hat{H} | \psi_j \rangle = \left\langle \psi_i \bigg| \frac{\partial V_{\text{local}}}{\partial R_{r,\mu}} \bigg| \psi_i \rightangle + \left\langle \psi_i \bigg| \frac{\partial V_{\text{nonlocal}}}{\partial R_{r,\mu}} \bigg| \psi_j \right\rangle,
\]

where the notation \( r \) is explicitly given as the atomic index, and \( R_{r,\mu} \) denotes the atomic position in the \( \mu \) direction. The contribution from the local part of the pseudopotential is

\[
\left\langle \psi_i \bigg| \frac{\partial V_{\text{local}}}{\partial R_{r,\mu}} \bigg| \psi_j \right\rangle = -Q \sum_G iG_\mu V_{\text{local}}^r(G) Y_{\epsilon j}(G) p_{ij}^r(G),
\]

where \( Q \) is the supercell volume, \( Y_{\epsilon j}(G) \) is the structure factor \( \exp(-iG \cdot R_j) \), and \( p_{ij}^r(G) \) is the Fourier transform of the contracted density \( \psi_i(\mathbf{r}) \psi_j(\mathbf{r}) \).

The contribution from the nonlocal part of the pseudopotential is

\[
\left\langle \psi_i \bigg| \frac{\partial V_{\text{nonlocal}}}{\partial R_{r,\mu}} \bigg| \psi_j \right\rangle = -\frac{1}{\sqrt{Q}} \sum_G P_{ij}^r(G) Y_{\epsilon j}(G) c_i^r(G),
\]

where \( D_{ij}^a \) is the overlap between the projector \( P_{ij}^a(G) \) of the nonlocal part of the pseudopotential and the KS orbital \( c_i \) (i.e., the Fourier transform of \( \psi_i \)),

\[
D_{ij}^a = \frac{1}{\sqrt{Q}} \sum_G P_{ij}^a(G) Y_{\epsilon j}(G) c_i^r(G).
\]

The corresponding derivative is calculated as

\[
\frac{\partial D_{ij}^a}{\partial R_{r,\mu}} = -\frac{1}{\sqrt{Q}} \sum_G iG_\mu P_{ij}^a(G) Y_{\epsilon j}(G) c_i^r(G).
\]

The matrix elements can be calculated in a way very similar to the calculation of forces acting on the nuclei. For the checking purpose, we can calculate the diagonal elements and compare the trace (weighted by the occupation number) with the pseudopotential contributions to the forces. In practical calculations, there is no need to calculate such matrix elements, since only transition pairs contribute to NACs. It is also worth mentioning that the symmetry operations in calculating forces as implemented in ABINIT should not be applied to NACs.

IV. RESULTS AND DISCUSSIONS

To show the performance of our method, we have applied it to study several molecular applications, including the extensively studied ci in the H\(_3\) system, the Rydberg transitions in H\(_2\), and the charge-transfer excitation in the collision of atomic hydrogen with B\(^{2+}\).

A. Approaching ci of the H\(_3\) system: \( \theta \rightarrow 0 \) in hyperspherical coordinates

It is well known that a ci point exists between the ground (\( ^1A' \)) and the first excited (\( ^2A' \)) electronic potential energy surfaces of the H\(_3\) system at C\(_{3v}\) geometries, i.e., equilateral triangle configurations. Abrol \textit{et al.} \(^{35}\) have done intensive work to calculate accurate NACs for H\(_3\), using hyperspherical coordinates (\( \rho, \theta, \phi \)) in which the locations of ci correspond to the coordinates at \( \theta=0 \). (The detailed explanation of the coordinates nomenclature can be found in Ref. 35.) Therefore, we would like to examine the performance of our method when approaching ci of the H\(_3\) system, as Baer \(^{25}\) did in his real-time TDDFT calculations. In Fig. 1, we present the results of TDDFT within LR for two in-plane components of NACs on the second H atom at fixed hyperspherical coordinates \( \rho=2.5 \) bohrs and \( \phi=120^\circ \), as a function of \( \theta \) when \( \theta \) decreases from \( 5^\circ \) to \( 1^\circ \). We have used the same supercell (16 bohrs) as Baer did. It can be seen that our result agrees well with his real-time TDDFT calculation, which is quantitatively good compared with the multiconfiguration self-consistent-field/configuration interaction (MCSCF/CI) calculations of Abrol \textit{et al.} As the ci point is approached, the agreement quickly degrades. We have found that it is necessary to use a sufficiently large supercell in the vicinity of ci since the excitation energy is very small. Therefore, a sufficiently large supercell (\( 32 \times 30 \times 32 \) [bohrs])\(^3\) has been used in the later calculations within either LR or MLR for \( \theta \approx 1^\circ \). The results are shown in Fig. 2. It is exciting to see that even when \( \theta \) is decreased to as small as 0.1°, the calculated NACs within MLR still agree with the reference data of Abrol \textit{et al.} in reasonable accuracy. In contrast, the

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FIG. 1. The Cartesian components of NACs on the second atom as a function of the hyperspherical angle \( \theta \), computed by different methods: Our TDDFT method within LR (empty circles), the real-time TDDFT approach by Baer (Ref. 23) (empty triangles), and the MCSCF/CI method by Abrol \textit{et al.} (filled circles).
LR result fails in the small \( \theta \) region: Even the relative signs of NACs, which do not pose a problem in MLR calculations, cannot be correctly determined within LR.

The good performance of MLR can be traced back to its ability in calculating excitation energies. In Fig. 3, we compared excitation energies from different calculation methods. The LR result quickly loses accuracy at small \( \theta \) region, while the MLR one is well behaved and shows a trend toward zero when \( \theta \rightarrow 0 \), which is similar to that of the reference data.\(^{35} \)

As a result, the adiabatic potential energy curves from MLR exhibit a trend of crossing at the ci point \((\theta=0^\circ)\), as shown in Fig. 4, in contrast to the failure of LR calculations.

Furthermore, it is found that MLR excels more than LR in obtaining DFT-SCF convergence as \( \theta \) is approached in the \( \text{H}_3 \) system. At fixed hyperspherical coordinates \( \rho=3.0 \) bohrs and \( \phi=140^\circ \), there is difficulty in obtaining SCF convergence in LR calculations when \( \theta < 1^\circ \), while it is at ease to get convergent results in MLR calculations. In Fig. 5, we show the \( z \) components of NACs on the third atom. The LR result agrees well with the reference data of Abrol \textit{et al.}\(^{35} \) when \( \theta > 1^\circ \); however, it is not available as \( \theta < 1^\circ \) due to the difficulty in achieving SCF convergence for the ground state. In comparison, the MLR calculations have no such problems and the computed NACs agree reasonably well with the reference data. This can be understood from the equal occupation of the donor/acceptor orbitals in the midexcited state configuration of the \( \text{H}_3 \) system, which facilitates the SCF calculation near the degeneracy point.

### B. Quantization of NACs in the \( \text{H}_3 \) system: The Jahn-Teller effect

For the studies on an infinitely small region surrounding the ci point of the \( \text{H}_3 \) system, employing either perturbation theory\(^{36} \) or \textit{ab initio} wave-function-based method\(^{37} \) leads to a
quantized angular NAC between the 1^2A' and 2^2A' states, namely,

\[ A_{12, \varphi} = A_{12, x} \frac{dx}{d\varphi} + A_{12, y} \frac{dy}{d\varphi} = \frac{1}{2} \]

which can be analytically verified from the Jahn-Teller model. Here \( \varphi \) is the radial angle of the atom moving on the contour surrounding the ci point, as shown in Fig. 6. Choosing the ci point as the coordinate origin, we can write

\[ A_{12, \varphi} = -q(A_{12, x} \sin \varphi + A_{12, y} \cos \varphi), \]

where \( q \) is the radius of the contour and the Cartesian components of NACs correspond to those on the rotating atom.

In Fig. 7, we show that our TDDFT calculations on NACs of the H_3 system \( R_{HH} = 1.044 \text{ Å}, q = 0.3 \text{ Å} \), within either LR or MLR, give consistent results with the reference data calculated at the state-average complete active-space self-consistent-field (CASSCF) level.\(^{38}\) Performing similar calculations by using different values of \( R_{HH} \) and \( q \), we find that the LR result degrades as \( q \) becomes smaller, while MLR still works well, as shown by Fig. 8 (corresponding to \( R_{HH} = 0.74 \text{ Å}, q = 0.1 \text{ Å} \)) and Fig. 9 (corresponding to \( R_{HH} = 1.044 \text{ Å}, q = 0.01 \text{ Å} \)). The MLR results well reproduce the features of NACs along the contour.\(^{39}\) The wiggly behavior of NACs is observed as the atom moves on the contour; when \( q \) becomes smaller, the oscillating amplitude decreases and becomes closer to the quantized value of \( \frac{1}{2} \), which is especially prominent in the case of \( q = 0.01 \text{ Å} \).
C. Rydberg and charge-transfer excitations

Besides the region close to \( \mathrm{ci} \), MLR is also expected to improve TDDFT performance on calculation of NACs between the ground state and Rydberg/charge-transfer states, since it can give more accurate excitation energies in such cases. In Fig. 10, we show radial NACs between the ground \((X^1\Sigma^+)_g\) and the Rydberg \((E\,^1\Sigma^+)_g\) state of the \( \text{H}_2 \) molecule as a function of the internuclear distance \( R \), calculated by TDDFT within either LR (empty triangles) or MLR (empty circles). The reference data (Ref. 42) are shown by filled circles.

D. Discussions on several technical points of TDDFT calculations

The above TDDFT calculations in the Casida formalism show that our method works well for various molecular applications, especially through the use of MLR. However, there may be some conditions difficult to be dealt with at present. One is the case of large internuclear distance, to which DFT/LDA calculations often give unphysical results (known as the dissociation problem). MLR seems to have no improvement on this aspect. The other condition is, still, in the very vicinity of \( \mathrm{ci} \), since degeneracy poses a practical problem to the dissociation problem of diatomic molecules in DFT/LDA. 40–41 It is clearly seen that the MLR result agrees well with the reference data calculated from \textit{ab initio} wave functions, \textit{42} while the LR result is underestimated. We point out here that in our MLR calculations within ALDA (spin unpolarized), the ordering of \( \sigma_g \) and \( \sigma_u \) orbitals changes with respect to different \( R \) values. It can also differ for the ground and midexcited states. Therefore, it is necessary to examine carefully the orbital diagram by plotting the orbital wave functions in MLR calculations.

Figure 11 shows the radial NACs between the ground \((1\,^1\Sigma^+)_g\) and the charge-transfer \((2\,^1\Sigma^+)_u\) state of the \( \text{HB}^+ \) as a function of the internuclear distance \( R \), calculated by TDDFT within either LR or MLR. The center of mass of the system is chosen as the coordinate origin. It is clearly seen that the MLR result agrees well with the reference data calculated from the quantum-mechanical molecular-orbital close-coupling method, \textit{43} while the LR result is overestimated. Concerning the systematic underestimation of Rydberg and charge-transfer excitation energies by TDDFT-LR within ALDA without correction of the exchange-correlation potential, \textit{44–46} we would like to emphasize here that NACs can be either underestimated or overestimated by TDDFT-LR in these conditions.

V. CONCLUSION

In summary, we have presented an efficient method to compute nonadiabatic couplings between the electronically ground and excited states of molecules, within the framework of time-dependent density functional theory in frequency domain. The formulation is rigorous and similar to the derivation of oscillator strength in the Casida formalism. The adiabatic LDA/LSDA gives results in reasonable accuracy as long as the conical intersection is not approached too closely, which is consistent with real-time TDDFT calculations. To achieve better performance within LDA/LSDA, we have incorporated modified linear response theory through use of the ground-state-component separation scheme. In this scheme, the excitation energy is computed from the response of the midexcited state, while the nonadiabatic strength term (the numerator in the formula of nonadiabatic couplings) is obtained from the response of the pure-state configuration.
This scheme has been demonstrated to work well either in the vicinity of conical intersections of the H$_3$ system, reproducing the quantized nonadiabatic couplings due to the Jahn-Teller effect, or for the Rydberg transition in H$_2$ and the charge-transfer excitation in HB$^{2+}$. At present, our test systems are restricted to several simple systems. More extensive work in various molecular systems is expected to be carried out in the future.

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